



05536501A

United States Patent [19][11] **Patent Number:** **5,536,501****Emerson et al.**[45] **Date of Patent:** **Jul. 16, 1996**[FLAVONOID] AROMATIC[54] **USE OF FLAVONOALDEHYDES AS
INSECTICIDES AND FOR KILLING
ARACHNIDS**[75] **Inventors:** **Ralph W. Emerson; Bradford G.
Crandall, Jr., both of Davis, Calif.**[73] **Assignee:** **ProGuard, Inc., Suisun City, Calif.**[21] **App. No.:** **366,974**[22] **Filed:** **Dec. 30, 1994**[51] **Int. Cl.⁶** **A01N 35/00**[52] **U.S. Cl.** **424/405; 424/70.1; 424/401;
424/408**[58] **Field of Search** **424/401, 70.1,
424/84, 403-405; 514/698**[56] **References Cited****U.S. PATENT DOCUMENTS**

2,465,854	3/1949	Dorman et al.	167/30
3,236,869	2/1966	Thompson	260/405.5
4,193,984	3/1980	Kydonieus	424/16
4,402,950	9/1983	Wolf et al.	424/195
4,477,361	10/1984	Sperti	252/106
4,978,686	12/1990	Sotome	514/698
5,149,715	9/1992	Armstrong et al.	514/701

Amend the title on the cover page and at col. 1, lines 1-3 as follows:

USE OF [FLAVONOID] AROMATIC ALDEHYDES AS INSECTICIDES AND
FOR KILLING ARACHNIDS



JS005536501A

[11] Patent Number: 5,336,501

[45] Date of Patent: Jul. 16, 1996

5,166,317 11/1992 Wallace et al. 530/350
5,202,247 4/1993 Kilburn 435/195
5,340,731 8/1994 Kilburn et al. 435/179

FOREIGN PATENT DOCUMENTS

94/24158 10/1994 WIPO .

OTHER PUBLICATIONS

Casey & Dobb, *Enzyme Microb. Technol.* (1992)
14:739-747.

Yuan et al., *Fundamental & Applied Toxicol.* (1993)
20:83-87.

Primary Examiner—Thurman K. Page

Assistant Examiner—Sharon Howard

Attorney, Agent, or Firm—Rae-Venter and Associates

[57] ABSTRACT

Methods and compositions based upon natural flavenoid aldehydes are provided, which find use as pesticides. The pesticides are formulated in a variety of ways, including dusts, sprays, shampoos and soaps, and can be bound to a solid support or provided as bait or directly impregnated into organic matter infested by or susceptible to infestation by a target pest.

[flavonoid] aromatic

16 Claims, No Drawings

Replace the text of the abstract with the following:

Methods and compositions based upon natural [flavonoid] aromatic aldehydes are provided, which find use as pesticides. The pesticides are formulated in a variety of ways, including dusts, sprays, shampoos and soaps, and can be bound to a solid support or provided as bait or directly impregnated into organic matter infested by or susceptible to infestation by a target pest.

5,536,501

[FLAVONOID] 1, AROMATIC

USE OF FLAVENOID ALDEHYDES AS
INSECTICIDES AND FOR KILLING
ARACHNIDS

CROSS-REFERENCE TO RELATED
APPLICATIONS

1994 This application is related to applications Ser. No. 08/366,
973, filed Dec. 30, 1994, and Ser. No. 08/367,082 filed Dec.
30, 1994 which applications are hereby incorporated by
reference.

INTRODUCTION

1. Technical Field

The present invention is related to the biocontrol of
insects and arachnids using [flavonoid] aldehydes. aromatic

2. Background

Organic matter, including decaying organic matter, is
colonized by a variety of organisms, many of which are
dependent upon a particular organic material as a source of
nutrients. The colonizing organisms include a variety of
insects and arachnids, some of which spread disease and/or
damage the material which they colonize. The insects and
arachnids which colonize particular organic materials
include those species which are symbiotic with bacteria,
such as cockroaches, fleas, termites and spider mites; the
host organism cannot survive without the symbionts.

A variety of compositions are used for controlling insect
and arachnid pests. However, the wide-spread use of pesti-
cides has resulted in the development and evolution of
resistant pests, as well as growing environmental and health
care concerns. A highly visible ecological-environmental
activist community and public regulatory agencies have
resulted in fewer and fewer pesticide registrations and,
consequently, less related research and development. It
therefore is of interest to identify and/or develop, "biora-
tional" formulations which have lower animal and environ-
mental toxicities yet are effective in controlling insect and
arachnid pests.

RELEVANT LITERATURE

A method of protecting crops from attack of pests includ-
ing insects using a composition comprising cinnamic alde-
hydes and requiring an antioxidant is disclosed in U.S. Pat.
No. 4,978,686. Protection of crops against insect pests by
applying an aqueous composition containing a cinnamalde-
hyde is disclosed in French patent application 2529755. U.S.
Pat. No. 2,465,854 describes an insecticidal composition
containing a cinnamic aldehyde derivative.

U.S. Pat. No. 4,402,950 describes the deactivation of
viruses inside living human and animal organisms by appli-
cation of a terpene obtainable from aromatic plants by steam
application. The terpenes cited are: black pepper oil, cinna-
mon flour oil, cardamon oil, linallyl acetate, cinnamic alde-
hydes, safrol, caryon and cis/trans citraol. Antifungal-anti-
bacterial detergents containing cinnamic compounds are
reported in U.S. Pat. No. 4,477,361.

SUMMARY OF THE INVENTION

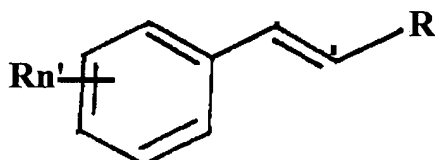
[flavonoid] The present invention provides a method for controlling
insect and arachnid pest populations through nutritional
mediation using flavonoid aldehydes. The method includes
the step of contacting a target pest with an amount of a
flavonoid aldehyde sufficient to control growth of the target
aromatic

Replace the paragraph beginning at col. 1, lines 16 with the following:

The present invention is related to the biocontrol of insects and arachnids using [flavenoid] aromatic aldehydes.

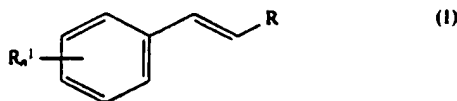
Replace the paragraph beginning at col 1, line 65 with the following:

The present invention provides a method for controlling insect and arachnid pest populations through nutritional mediation using [flavonoid] aromatic aldehydes. The method includes the step of contacting a target pest with an amount of an [flavonoid] aromatic aldehyde sufficient to control growth of the target pest. The aldehyde can be provided in a variety of formulations, including as a component of a trap which optionally contains a chemoattractant for the target pest. The growth modulating product has a formula shown in (1) below.



wherein R represents $-CH_2OH$ or $[CHO]$ $-CHO$ or $[H]$ $-H$; n is an integer from 0 to 3; and each R^1 independently represents $[OH]$ $-OH$, $-H$ or an organic substituent containing from 0 to 10 carbon atoms and from 0 to 5 heteroatoms, wherein the total number of carbon and heteroatoms in all R^1 substituents of said compound is no more than 15. These compounds include natural compounds such as cinnamaldehyde, coniferyl aldehyde, and closely related compounds. The invention finds use in controlling pest populations in areas of infestation, or areas susceptible to infestation. The method finds use in killing target pest populations.

pest. The aldehydes can be provided in a variety of formulations, including as a component of a trap which optionally contains a chemoattractant for the target pest. The growth modulating product has a formula shown in (1) below.



10 wherein R represents $\text{—CH}_2\text{OH}$, CHO or H ; n is an integer from 0 to 3; and each R^1 independently represents OH , —H , or an organic substituent containing from 0 to 10 carbon atoms and from 0 to 5 heteroatoms, wherein the total number of carbon and heteroatoms in all R^1 substituents of said
15 compound is no more than 15. These compounds include natural compounds such as cinnamaldehyde, coniferyl aldehydes, and closely related compounds. The invention finds use in controlling pest populations in areas of infestation, or areas susceptible to infestation.

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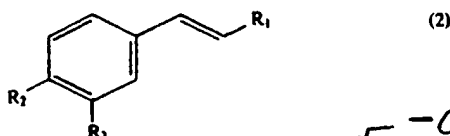
BRIEF DESCRIPTION OF SPECIFIC EMBODIMENTS

Flavonoid Methods and compositions are provided for obtaining and/or maintaining an area substantially free of pests such as insects and arachnids using flavonoid aldehydes to biocontrol the area. By "biocontrol" is intended control of pests via direct pesticidal activity on a target pest or by indirect pesticidal activity by antibacterial action on symbiont bacteria resident in the target pest. aromatic

30 A target pest colonizing an area is contacted with a natural product. By "colonizing" is intended association of a pest with an area which provides access to organic matter which serves as a source of nutrients for the pest, typically essential nutrients such as amino acids, particularly methionine. By
35 "natural product" is intended an organic compound of natural origin that is unique to one organism, or common to a small number of closely related organisms, and includes secondary metabolites provided by the organic matter. The
40 natural products can be isolated from a natural source, be wholly or partially synthetic, or be produced by recombinant techniques. The amount of natural product that is provided, either applied to organic matter colonized by the target pest or as bait, will depend upon the degree of infestation of the
45 area and to some extent upon the formulation and the specific compounding used and therefore must be empirically determined for best results.

50 The compositions and methods of the subject invention offer several advantages over existing compositions and methods, including that they are safe for use around humans, animals and food sources. Additionally, the compositions can be used to impregnate organic matter which serves as a nutrient source for a target pest and/or can be provided bound to a solid support which itself is non-toxic to animals,
55 including humans.

The subject formulation is as shown in formula (1) above. A preferred formulation is shown in formula (2) below.



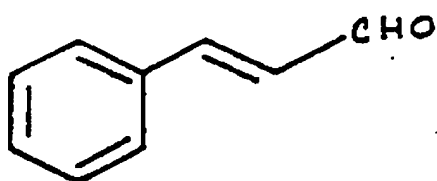
65 Wherein R_1 represents —CHO , R_2 represents —OH or an organic substituent containing from 1 to 10 carbon atoms, and R_3 represents a methoxy group, —H , or an organic

Replace the paragraph beginning at col. 2, line 24 with the following:

Methods and compositions are provided for obtaining and/or maintaining an area substantially free of pests such as insects and arachnids using [flavenoid] aromatic aldehydes to biocontrol the area. By "biocontrol" is intended control of pests via direct pesticidal activity on a target pest or by indirect pesticidal activity by antibacterial action on symbiont bacteria resident in the target pest.

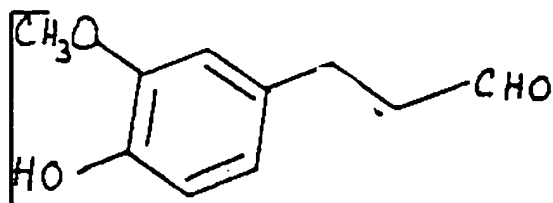
Replace the paragraph beginning at col. 2, line 65 with the following:

Wherein R_1 represents $-CHO$, R_2 represents $[OH]$ $-OH$, $-H$ or an organic substituent containing from 1 to 10 carbon atoms, and R_3 represents a methoxy group, $-H$, or an organic substituent containing from 1 to 10 carbon atoms. Of particular interest are [flavonoid aldehydes, particularly] aromatic aldehydes. Examples of aromatic aldehydes of use in the present invention are cinnamic aldehyde ((3) below).

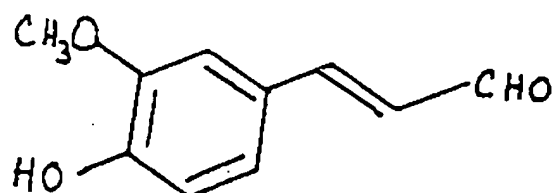


(3)

and coniferyl aldehyde ((4) below).



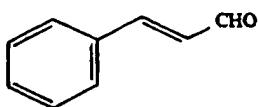
(4)



(4)

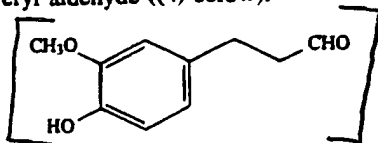
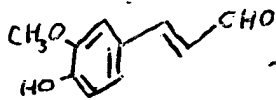
A number of the aromatic and aliphatic aldehydes which may find use in the subject invention, such as benzaldehyde, acetaldehyde, cinnamaldehyde, piperonal, and vanillin are generally regarded as safe (GRAS) synthetic flavoring agents (21 CFR §172.515). The general formula of these compounds is shown above as (1).

[Flavonoid] substituent containing from 1 to 10 carbon atoms. Of particular interest are flavonoid aldehydes, particularly aromatic aldehydes. Examples of aromatic aldehydes of use in the present invention are cinnamic aldehydes ((3) below)



(3) 5

and coniferyl aldehyde ((4) below).



10

(4)

A number of the aromatic and aliphatic aldehydes which may find use in the subject invention, such as benzaldehyde, acetaldehyde, cinnamaldehyde, piperonal, and vanillin are generally regarded as safe (GRAS) synthetic flavoring agents (21 CFR §172.515). The general formula of these compounds is shown above as (1).

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The compounds may be used either alone or in combination with other active or inactive substances and may be applied by spraying, pouring, dipping, in the form of concentrated liquids, solutions, suspensions, powders and the like, containing such concentration of the active compound as is more suited for a particular purpose at hand. They may be applied, for example, in the form of dilute solution, in a suitable solvent directly to an area of pest infestation or an area susceptible to infestation or bound to a solid support for application in powder form or in a "trap".

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For use as a means of cleansing a surface, such as a carpet, pet bedding, pet fur and the like, although the aldehyde can be formulated alone as an aqueous solution, it also can be prepared as a soap or a detergent. Detergents which can be used include anionic detergents such as those described in U.S. patent application Ser. No. 4,978,686. Additional components such as an aqueous preparation of a salt of a polyprotic acid such as sodium bicarbonate, sodium sulfate, sodium phosphate or sodium biphosphate can be included in the formulation, to increase the pesticidal properties of the formulation. The resulting emulsion is diluted to an appropriate concentration for use, and is additionally provided as a formulation suitable for the intended application, i.e. carpet shampoo, detergent, or animal shampoo or soap including shampoo or soap for human use.

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For applications where the formulation is to be used as a trap or as bait for a particular pest, the formulations of the subject invention can be sprayed directly in an area of infestation or they can be bound to a solid support or encapsulated in a time release material. Where a solid carrier is used, materials which can lead to oxidation of the active aldehydes should be avoided. Examples of delivery systems include starch-dextran, and the like. See Yuan et al., *Fundamental and Applied Toxicology* (1993) 20:83-87 for examples of delivery systems.

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In addition to the specific compounds of the formulas (1), (2) and (3), set forth above, derivatives of any of these compounds that produce a compound of the formula identified above upon action of a biological system on the derivative are considered to be equivalent to compounds of the invention. Thus application of precursor compounds to pests which can metabolize the precursors to produce a specific compound identified above would be equivalent to the practice of the present invention. Biological conversion of precursor compounds into flavonoid aldehydes is described in, for example, U.S. patent application Ser. No. 5,149,715 and references cited therein. See also Casey and Dobb *Enzyme Microb. Technol.* (1992) 14: 739-747.

55

60

65

aromatic

[Flavonoid]

Replace the paragraph beginning at col. 3, line 55 with the following:

In addition to the specific compounds of the formulas (1), (2) and (3), set forth above, derivatives of any of these compounds that produce a compound of the formula identified above upon action of a biological system on the derivative are considered to be equivalent to compounds of the invention. Thus application of precursor compounds to pests which can metabolize the precursors to produce a specific compound identified above would be equivalent to the practice of the present invention. Biological conversion of precursor compounds into [flavonoid] aromatic aldehydes is described in, for example, U.S. Patent [Application Ser.] No. 5,149,715 and references cited therein. See also Casey and Dobb Enzyme Microb. Technol. (1992) 14: 739-747.

The method of the present invention is carried out by introducing into a target pest a sufficient amount of a pesticide to impair growth and/or viability of the target pest and thereby decrease the population of that pest in an area.

5 A formulation containing the pesticide is introduced to an area of infestation. For example, the formulation is sprayed on as a wet or dry formulation on the surface of organic material infected with a target pest, or organic material susceptible to infestation with a target pest. Alternately, the
10 formulation can be applied wet or dry to the an area of infestation where it can contact the target pest. In some instances, time-release formulations may find use, particularly for applications to animals, or areas which are subject to reinfestation, such as animal quarters.

15 The method of introducing of the subject pesticide into the target pest can be by direct ingestion by the target pest from a trap, or by feeding of a target pest on nutrient-providing organic matter treated with the pesticide. In some instances, the pesticide may be absorbed by the pest, particularly where the formulation provides for uptake by the
20 outer tissues of the pest, particularly a larval or other pre-adult form of the pest, such as a detergent formulation.

For some applications, such as infestations of cockroaches and termites, it is necessary to deliver the formulation to the location of the pest colony. When used in a solid
25 form or microencapsulated, the dosage used would typically be on the order of 1% to 35% on a w/w basis, the maximum loading to be determined as a function of shell material selected. Analytical chemical techniques are used to determine and optimize rate of release. For qualitative purposes, GC techniques can be used to determine the amount of aldehydes released. The samples of encapsulated (pelletized) product are sampled at different time periods to measure release. Alternatively, volatile gases released from the
35 formulation can also be analysed. For measuring the activity of spray or powder applications the stability of the formulations over time can also be evaluated by the GC methodology using techniques known to those skilled in the art. Methanol or alcohol extractions of the formulations also can be prepared and evaluated by HPLC analysis.

The aldehyde components can be coupled to a solid support, optionally through a linker such as a polysaccharidase binding domain, where the solid support is a polysaccharide such as cellulose, particularly microcrystalline cellulose. The preparation of [cellulase] binding domains is
45 described in U.S. patent [application Ser.] Nos. 5,340,731; 5,202,247 and 5,166,317. The aldehydes can be coupled to the binding domains, with or without a cleavable bond, using methods well known to those skilled in the art. These
50 formulations can be used to directly impregnate a surface comprising the appropriate polysaccharide, for example where the surface is a cellulose, such as paper or wood, a [cellulase/binding domain] is used. As an example, the [flavonoid/aldehyde [cellulase] binding domain] composition can be used to impregnate wood which is subject to or already
55 infested with termites. In other applications, the aldehyde-[cellulase] binding domain composition can be bound to paper as a trap or to microcrystalline cellulose wherein the granules can be transported back to the colony. Optionally, the bait or
60 trap additionally can include a chemoattractant for the target pest, such as putrescine for flies or cadavarine for cockroaches bound to the cellulose support via a [cellulase] binding domain. Other examples of chemoattractants are well known to those skilled in the art.

65 In addition to providing bait or traps, infestations of target pests also can be treated using powder or detergent formulations, for example as a carpet shampoo to treat infestations

cellulose

bond

aromatic

cellulose

Replace the paragraph beginning at col. 4, line 41 with the following:

The aldehyde components can be coupled to a solid support, optionally through a linker such as a polysaccharidase binding domain, where the solid support is a polysaccharide such as cellulose, particularly microcrystalline cellulose. The preparation of [cellulase] cellulose binding domains is described in U.S. Patent [Application Ser.] Nos. 5,340,731; 5,202,247 and 5,166,317. The aldehydes can be coupled to the binding domains, with or without a cleavable bond, using methods well known to those skilled in the art. These formulations can be used to directly impregnate a surface comprising the appropriate polysaccharide, for example where the surface is a cellulose, such as paper or wood, a [cellulase] cellulose binding domain is used. As an example, the [flavenoid] aromatic aldehyde-[cellulase] cellulose binding domain composition can be used to impregnate wood which is subject to or already infested with termites. In other applications, the aldehyde-[cellulase] cellulose binding domain composition can be bound to paper as a trap or to microcrystalline cellulose wherein the granules can be transported back to the colony. Optionally, the bait or trap additionally can include a chemoattractant for the target pest, such as putrescine for flies or cadavarine for cockroaches bound to the cellulose support via a [cellulase] cellulose binding domain. Other examples of chemoattractants are well known to those skilled in the art.

of dust mites and fleas and other susceptible pests. The formulations of the subject invention generally are non-staining and additionally often impart a pleasant odor to the treated surface.

The formulations also can be used as powders, soaps or 5
detergents for treatment of infestations of animals or humans, including infestations with fleas and ticks. In some instances it may be necessary to adjust the treatment formulation so as to reduce any dermatological effects associated with the treatment. Generally, the formulations are safe 10
for ingestion and additionally, typically have positive organoleptic and olfactory characteristics.

The target pests include insects and arachnids, particularly those which colonize organic matter, more particularly organic matter which is an elicitor for the pest. By elicitor is 15
intended that the organic matter provides nutrients required by the pest. Examples of pests and the organic matter or habitat which provides their nutrients are as follows. *Musca domestica* (L.) and *Stomoxys calcitrans* (L.), decaying organic matter, particularly matter, which includes 20
putrescine; Aphaniptera (Siphonaptera), blood; Argas (Persicargas) arboreus (Ixodoidea: Argasidae), blood; Dictyoptera: Blattellidae, decaying organic matter; Isoptera: Rhinotermitidae, organic matter, particularly matter containing cellulose. Also of interest are mites, such as spider mites 25
(arthropoda), dust mites, mites which infect honey bees and a variety of other mites. It is a theory of the invention that many of the insects and arachnids which are susceptible to treatment with the subject formulations are those which harbor symbiotic bacteria in their gut. Accordingly, insects 30
and arachnids other than those listed which harbor symbiotic organisms can also be controlled with the subject formulations.

In order to determine the susceptibility of particular pests to the subject compositions, in vitro and in vivo tests such 35
as are described in the Examples can be used. As appropriate, the formulations also need to be evaluated for dermatological effects; it therefore is important where appropriate that at least one evaluation of the toxicity of the formulations be tested on animal hosts for the target pest or on animals 40
which may come in contact with a treated surface so that the dermatological effects can be tested for the dosage of pesticide used. Such dermatological sensitivity tests can be conducted using methods known to those skilled in the art.

The following examples are offered by way of illustration 45
and not by way of limitation.

EXAMPLES

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EXAMPLE 1

Protocol for Spider Mite

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Activity of cinnamic aldehyde and/or coniferyl aldehydes against two-spotted spider mite, *Tetranychus urticae* is determined as follows:

Petri Dish Bioassay

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Each petri dish (60 mm diameter) is treated with a specific rate of product (e.g. 10-1000 ppm) dissolved in water, and allowed to dry. Twenty specimens of each arthropod are put in each dish, (replicate 10 times). The mortality after three hours in contact with a treated petri dish, is compared to that 65
of arthropods in petri dishes treated only with diluent.

Plant Foliar Bioassay

Replace the paragraph beginning at col. 5, line 13 with the following:

The target pests include insects and arachnids, particularly those which colonize organic matter, more particularly organic matter which is an elicitor for the pest. By elicitor is intended that the organic matter provides nutrients required by the pest. Examples of pests and the organic matter or habitat which provides their nutrients are as follows. *Muscara domestica* [L.] and *Stomoxys calcitrans* [L.], decaying organic matter, particularly matter, which includes putrescine; *Aphaniptera* (*Siphonaptera*), blood; *Argas* (*Persicargas*) *arboreus* (*Ixodoidea: Argasidae*), blood; *Dictyoptera: Blattellidae*, decaying organic matter; *Isoptera: Rhinotermitidae*, organic matter, particularly matter containing cellulose. Also of interest are mites, such as spider mites (*arthropoda*), dust mites, mites which infect honey bees and a variety of other mites. It is a theory of the invention that many of the insects and arachnids which are susceptible to treatment with the subject formulations are those which harbor symbiotic bacteria in their gut. Accordingly, insects and arachnids other than those listed which harbor symbiotic organisms can also be controlled with the subject formulations.

Cotton plants are grown in 7.5 mm pot in potting soil in greenhouse. When plants reach 3 leaf stage, they are infested with 60 of the specified arthropod (6 replications). The mite is allowed to settle and feed. The plant is sprayed to runoff with a formulation containing 100 to 2000 ppm, or 0.1 to 2 g/l concentration of a test formulation. The plant is covered with a tall plastic cage (5 mm tall x 10 mm diameter). The mortality after three days of the mites on the plants sprayed with a test formulation is determined and compared with that of mites on plants sprayed only with water.

EXAMPLE 2

Treatment for Flies

In an air conditioned case measuring 1.5 m x 1.5 m x 1.5 m, 150 flies (*Musca domestica* [(1..)] and *Stomoxys calcitrans* [(1..)] are released and sprayed with 8 ml of test product. The test product contains 100 to 2000 ppm of cinnamic aldehyde and/or coniferyl aldehyde in an appropriate formulation. After 15 minutes exposure, the number of flies that are unable to fly are noted. All flies are transferred to a holding case with fresh air and allowed to recuperate for 20 hours. The number of dead flies are counted, and the percentage of flies killed with each formulation compared to that of no treatment and treatment with a formulation known to kill flies at a level of about 70%.

EXAMPLE 3

Treatment of Fleas

Petri Dish Bioassay

(Aphaniptera (Siphonaptera)) susceptibility is tested as follows. Petri dishes (60 mm diameter) are treated with a specific dose of product (100 to 2000 ppm) dissolved with water, and allowed to dry. Twenty specimens of the insect and twenty larvae of the insect each are put in separate dishes (replicate 10 times). The mortality of insect and larvae after thirty hours in contact with a treated plate is compared to that of insects and larvae treated only with the diluent, and treatment with a formulation known to kill fleas at a level of about 70%.

EXAMPLE 4

Treatment of Ticks

Petri dishes (80 mm diameter) are treated with a specific rate of product (e.g. 10 to 2000 ppm) dissolved in water and allowed to dry. Twenty five specimens of the arachnid (*Argas (Persicargas) arboreus* (Ixooldea: Argasidae)) are put in each dish, replicate 10 times. The mortality after 30 hours in contact with a treated plate is compared to that of arachnids in petri dishes treated only with the diluent, or with a formulation known to kill tick at a level of about 70%.

EXAMPLE 5

Treatment Of German Cockroaches

Topical application Bioassay

Adult male cockroaches (Dictyoptera, Blattellidae) are used to evaluate insecticidal activity of cinnamic aldehydes and/or coniferyl aldehydes by a topical application method. The topical application is made by an ISCO model M microapplicator. Cockroaches are anesthetized with CO₂ then treated with 1 ml formula containing 1 to 2000 ppm of cinnamic aldehydes and/or coniferyl aldehydes by plac-

aldehyde

Replace the paragraph beginning at col. 6, line 16 with the following:

In an air conditioned case measuring 1.5 m x 1.5 m x 1.5 m, 150 flies (*Musca domestica* [(1..)] and *Stomoxys calcitrans* [(1..)] are released and sprayed with 8 ml of test product. The test product contains 100 to 2000 ppm of cinnamic aldehyde and/or coniferyl aldehyde in an appropriate formulation. After 15 minutes exposure, the number of flies that are unable to fly are noted. All flies are transferred to a holding case with fresh air and allowed to recuperate for 20 hours. The number of dead flies are counted, and the percentage of flies killed with each formulation compared to that of no treatment and treatment with a formulation known to kill [files] flies at a level of about 70%.

ing a microdroplet of solution on the ventral aspect of the penultimate abdominal segment using a 27-gauge needle on a glass tuberculin syringe. Ten cockroaches are treated with each formula and the experiment replicated three to five times. Treated cockroaches are placed in glass jars (0.95 liter) provisioned with food, water and harborage. The number of dead or moribund cockroaches 24 h after treatment is counted and compared to ~~these~~ ^{those} untreated (diluent only) or treated with a formulation known to kill approximately 70% of a cockroach population.

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EXAMPLE 6

Treatment of Western Subterranean Termites
(Isoptera: Rhinotermitidae) Laboratory Bioassay

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Tray Bioassay

Sterilized play sand is treated with aqueous emulsions of each formula and component to provide 500 ppm deposits (wt./wt. sand). 500 g samples of sand are evenly spread ≤ 1 mm thick over a metal tray (50 by 30 cm) and sprayed with 65 ml of emulsion with an air brush at 1.9/0 g/cm² (28 psi) to obtain uniform treatments. Six examples for each formula and component are prepared. The treated sand is dried in a fume hood for 30 minutes and the insecticidal activity of each formula treated sand is determined by continuously confining termites to treated deposits for 24 h. Ten termites are exposed on 2.5 ml of treated sand in petri dishes (35 by 10 mm) in each of five replicates. Termites and petri dishes are held in a chamber maintained at 93% RH with a saturated sodium sulfate solution. The number of dead or moribund termites after 24 h exposure is determined. Termites are considered dead if unable to right themselves within 5 min. The effectiveness of the test formulation is compared to termites treated with diluent only or with a formulation known to kill termites at a level of about 70%.

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All publications and patent applications mentioned in this specification are indicative of the level of skill of those skilled in the art to which this invention pertains. All publications and patent applications are herein incorporated by reference to the same extent as if each individual publication or patent application was specifically and individually indicated to be incorporated by reference.

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The invention now having been fully described, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made thereto without departing from the spirit or scope of the appended claims.

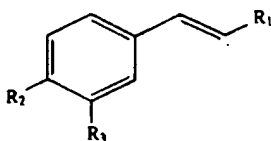
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What is claimed is:

1. A method for controlling an insect or an arachnid population, said method comprising:

contacting said insect or arachnid population with an effective pest growth modulating amount of a formulation comprising 0.01 g/l to 25 g/l of one or more compounds ~~or~~ having a formula

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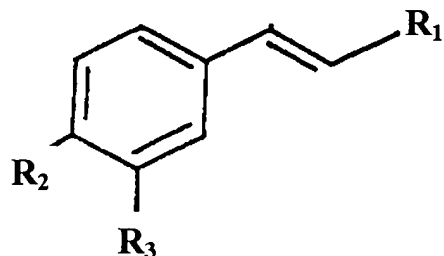
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wherein R₁ represents —CHO, R₂ represents —OH, \overline{H} or an organic substituent containing from 1 to 10 carbon atoms.

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Amend the Claims as follows:

1. (Amended) A method for controlling a pest population, said method comprising:
contacting said insect or arachnid population with an effective pest growth
modulating amount of a formulation comprising 0.01 g/l to 25 g/l of one or more
compounds having a formula



wherein R₁ represents -CHO, R₂ represents -OH, [H] -H or an organic substituent containing from 1 to 10 carbon atoms, and R₃ represents a methoxy group, [H] -H or an organic substituent containing from 1 to 10 carbon atoms; and wherein said formulation does not contain an antioxidant other than an antioxidant according to said formula.

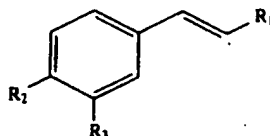
and R_3 represents a methoxy group, H or an organic substituent containing from 1 to 10 carbon atoms; and wherein said formulation does not contain an antioxidant other than an antioxidant according to said formula.

2. The method according to claim 1, wherein said effective insect or arachnid growth modulating amount is 2.5 g/l to 12.5 g/l.

3. The method according to claim 1, wherein said one or more compounds are of cinnamic aldehyde or coniferyl aldehyde.

4. The method according to claim 3, wherein said formulation provides for about 70% or greater kill of said insect or arachnid population.

5. The method according to claim 1, wherein said formulation is free of antioxidants other than compounds of a formula

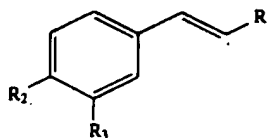


wherein R_1 represents —CHO , R_2 represents —OH , H or an organic substituent containing from 1 to 10 carbon atoms, and R_3 represents a methoxy group, H or an organic substituent containing from 1 to 10 carbon atoms.

6. The method according to claim 1, wherein said insect or arachnid population is selected from the group consisting of a cockroach, an ant, and a mite.

7. A composition suitable for use as bait for an insect or arachnid comprising:

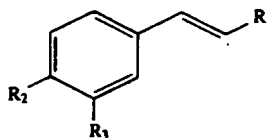
one or more compound having a formula



wherein R_1 represents —CHO , R_2 represents —OH , H or an organic substituent containing from 1 to 10 carbon atoms, and R_3 represents a methoxy group, H or an organic substituent containing from 1 to 10 carbon atoms, associated with a solid support.

8. A composition suitable for use as a shampoo or a soap, said composition comprising:

an insect or arachnid growth modulating amount of one or more compound of a formula

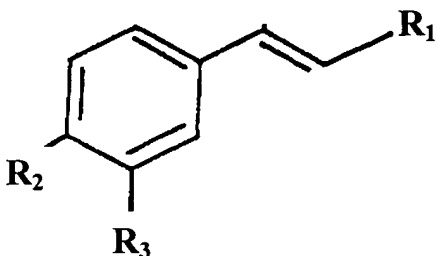


wherein R_1 represents —CHO , R_2 represents —OH , H or an organic substituent containing from 1 to 10 carbon atoms, in a soap or detergent formulation and R_3 represents a methoxy group, H or an organic substituent containing from 1 to 10 carbon atoms, to provide a kill of about 70% or greater of a target insect or arachnid population.

9. The composition according to claim 8, wherein said one or more compounds are cinnamic aldehyde or coniferyl aldehyde.

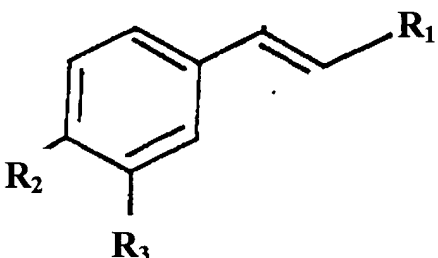
wherein said compound is not cinnamic aldehyde

5. (Amended) The method according to Claim 1, wherein said formulation is free of antioxidants other than compounds of a formula



wherein R₁ represents -CHO, R₂ represents -OH, [H] -H or an organic substituent containing from 1 to 10 carbon atoms, and R₃ represents a methoxy group, [H] -H or an organic constituent containing from 1 to 10 carbon atoms.

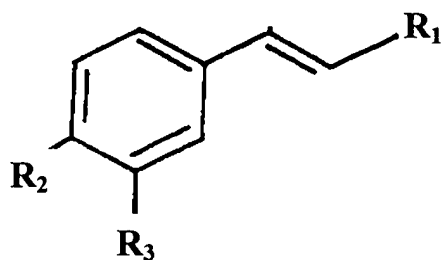
7. (Amended) A composition suitable for use as bait for insect or arachnid comprising: one or more compound having a formula



wherein R₁ represents -CHO, R₂ represents -OH, [H] -H or an organic substituent containing from 1 to 10 carbon atoms, and R₃ represents a methoxy group, [H] -H or an organic substituent containing from 1 to 10 carbon atoms, wherein said compound is not cinnamic aldehyde, associated with a solid support.

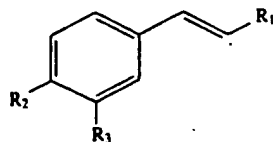
8. (Amended) A composition suitable for use as a shampoo or a soap, said composition comprising:

an insect or arachnid growth modulating amount of one or more compound of a formula



wherein R_1 represents $-CHO$, R_2 represents $-OH$, $[H]$ $-H$ or an organic substituent containing from 1 to 10 carbon atoms, in a soap or detergent formulation and R_3 represents a methoxy group, H or an organic substituent containing from 1 to 10 carbon atoms, to provide a kill of about 70% or greater of a target insect or arachnid population.

10. The composition according to claim 9, wherein said composition is free of antioxidants other than compounds of a formula

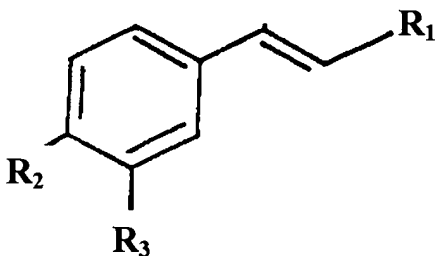


wherein R_1 represents $-\text{CHO}$, R_2 represents $-\text{OH}$, [H] or an organic substituent containing from 1 to 10 carbon atoms, and R_3 represents a methoxy group, [H] or an organic substituent containing from 1 to 10 carbon atoms.

11. The composition according to claim 10, wherein said composition comprises compounds of cinnamic aldehyde and coniferyl aldehyde.

12. A composition according to claim 7, wherein said solid support comprises cellulose.

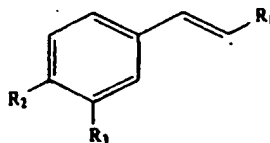
10. (Amended) The composition according to Claim 9, wherein said formulation is free of antioxidants other than compounds of formula



wherein R_1 represents $-CHO$, R_2 represents $-OH$, $[H]$ $\underline{-H}$ or an organic substituent containing from 1 to 10 carbon atoms, and R_3 represents a methoxy group, $[H]$ $\underline{-H}$ or an organic substituent containing from 1 to 10 carbon atoms.

12. (Amended) A composition according to Claim 7 or 17, wherein said solid support comprises cellulose.

13. A composition according to claim 12, wherein said one or more compound of the formula



10 wherein R_1 represents $-\text{CHO}$, R_2 represents $-\text{OH}$, $-\text{H}$ or an organic substituent containing from 1 to 10 carbon atoms, and R_3 represents a methoxy group, $-\text{H}$ or an organic substituent containing from 1 to 10 carbon atoms, is associated reversibly with said cellulose.

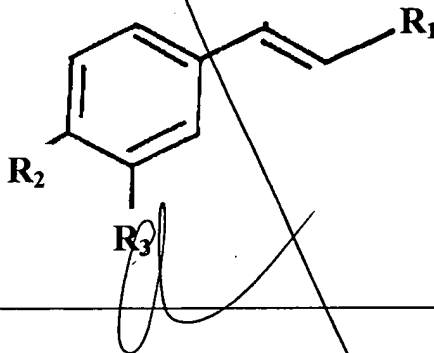
15 14. A composition according to claim 12, wherein said associated is via a cellulose binding domain.

15 15. A composition according to claim 7, wherein a chemoattractant for said insect or arachnid is associated with said solid support.

20 16. The composition according to claim 7, wherein said solid support is enclosed in a housing having means of ingress and egress for said insect or arachnid.

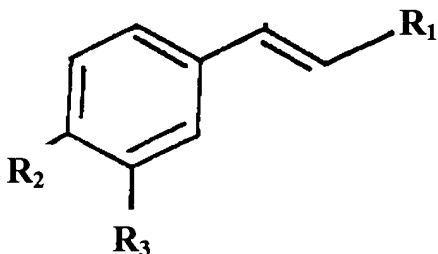
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17. (New) A composition comprising:
one or more compound having a formula



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wherein R_1 represents $-\text{CHO}$, R_2 represents $-\text{OH}$, $-\text{H}$ or an organic substituent containing from 1 to 10 carbon atoms, and R_3 represents a methoxy group, $-\text{H}$ or an organic constituent containing from 1 to 10 carbon atoms, wherein said compound is coupled to a solid support.

13. (Amended) The composition according to Claim 12, wherein said one or more compound of the formula



wherein R₁ represents -CHO, R₂ represents -OH, [H] -H or an organic substituent containing from 1 to 10 carbon atoms, and R₃ represents a methoxy group, [H] -H or an organic substituent containing from 1 to 10 carbon atoms, is associated reversibly with said cellulose.

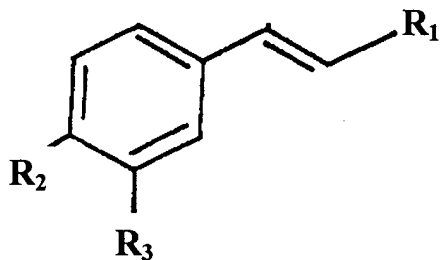
14. (Amended) A composition according to Claim 12, wherein said association is via a [cellulase] cellulose binding domain.

15. (Amended) A composition according to Claim 7 or 17, wherein said solid support is enclosed in a housing having means of ingress and egress for said insect or arachnid.

16. (Amended) The composition according to Claim 7 or 17, wherein said solid support is enclosed in a housing having means of ingress and egress for said insect or arachnid.

Add claim 17 as follows:

17. (New) A composition comprising:
one or more compound having a formula



wherein R₁ represents -CHO, R₂ represents -OH, -H or an organic substituent containing from 1

to 10 carbon atoms, and R_3 represents a methoxy group, -H or an organic constituent containing from 1 to 10 carbon atoms, wherein said compound is coupled to a solid support.